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**Keywords**
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# PREPARATION OF RARE EARTH METALS

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June 1951

Ames Laboratory

Technical Information Service, Oak Ridge, Tennessee

ABSTRACT

The production of over 400 grams of pure gadolinium metal by reduction of the anhydrous chloride by calcium in tantalum vessels is described; yields were over 97%. The use of the same techniques in an attempt to prepare yttrium metal were partially successful.

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# INTRODUCTION

The rare earth elements constitute a group of fourteen members which are, for reasons noted below, remarkably similar in both their physical and chemical properties. Since there was no place for these elements in the older periodic tables, they were grouped in the space allotted to lanthanum. Lanthanum, yttrium and scandium have atomic structures similar to, and always occur in, mixtures of rare earths as found in nature; lanthanum is usually included in the rare earth series on the basis of its chemical properties. Later, the true rare earths, which have atomic numbers from 58 through 71, were assigned a special place in the periodic tables and are now commonly called the lanthanide series. As noted in the historical section of this thesis, most of the rare earths had been discovered by 1900 and their properties studied by the methods then available.

In the period since 1900, the advances in chemical and physical methods greatly clarified the electronic structures of these elements and showed some of the reasons for the existence of this group of elements with very similar properties. All of these elements have their lower orbitals filled through the 4d level, and the differences between them is due to the manner in which their 4f and 5d orbitals are occupied. Between these levels are the 5s and 5p orbitals which tend to shield the 4f level from external fields. The electronic configuration of a neutral gaseous atom of lanthanum, which is often considered as the first member of this group, is $4f^0\ 5d^1\ 6s^2$ (1). Continuing through this group, the 4f orbital is gradually filled until it contains 14 electrons, but only lanthanum, gadolinium, terbium and lutetium have a 5d electron.

The 5d and 6s electrons are involved in the bonding orbitals in the chemical compounds of the rare earths; in ionic compounds they are held by the negative ions. In these cases, the relative stability of the 4f level is such that it is occupied by a regularly increasing number of electrons, from zero for lanthanum up to fourteen in the case of lutetium, without the variations evidenced in the normal gaseous atom. In metals the valence electrons are in the electronic conduction bands and the relative stability of the 4f and 5d levels may be modified giving rise to slight deviations in the physical properties of the metals.

The principal difference in the rare earth elements is in the population of the 4f orbital which is screened by the completed 5s and 5p orbitals. This screening action prevents the 4f electrons from taking part in chemical combination. The chemical similarity of these elements is explained on the basis of their identical outer electronic structures since only the 5d and 6s electrons are involved in the bonding orbitals.

The normal valency state common to the rare earth group is tri-positive.

In the rare earth group, the increasing nuclear charge with a nearly uniform outer electronic structure results in a slight decrease in atomic radius as the atomic number increases (2). The slight differences in the properties of these elements can in part be attributed to this shrinkage in the atomic radius. The gradual change of this one parameter makes the rare earth group an interesting one which not only serves to correlate the various properties of metals with their atomic and molecular structures, but also should be helpful in advancing theories concerning metals.

The purpose of the research presented in this thesis was the preparation of very pure gadolinium and yttrium metals. The metallurgical process previously reported by Daane (3) was extended to these metals and the quantity of material per reduction was increased.

This work is a continuation of the over-all program of preparation of pure metals which was one of the major contributions of these laboratories to the Manhatten Project (4,5). During this wartime period, more than 1,000 pounds of 96% cerium metal (6) were produced. This cerium metal was required in order to study the chemical and physical properties of the rare earth elements because they constitute a large percentage of the products of atomic fission. The metal was prepared by the reduction of cerous chloride by calcium in the presence of iodine; the resulting calcium iodide furnished the necessary heat to cause the metal to agglomerate. The container for the reaction was a steel bomb lined with jolt packed or sintered magnesium oxide or dolomitic oxide. Any volatile impurities were removed in the vacuum casting operation.

In order to prepare very pure metals, it was necessary to have as a starting material the corresponding pure rare earth compounds. Methods worked out in these laboratories (7,8), involving the adsorption on an Amberlite or a high capacity resin bed and elution with citrate solutions at the appropriate pH values, provided the rare earth compounds of the necessary purity. The procedure used to prepare impure metallic cerium had to be modified in order to procure very pure metals. The modifications introduced into this process were employment of an inert atmosphere in the bomb-loading operation; the use of purer refractories and reactants; and the use of higher vacua in the casting operation. This modified technique has been used to prepare very pure cerium, lanthanum, neodymium, praseodymium and didymium in 160-gram batches in yields over 98% (9). The principal objections to this method are: (1) the lower yields obtained when a smaller charge is used; (2) the recovery of rare earth salts from unsuccessful runs was difficult because the reaction mixture soaked into the porous bomb liner; and (3) the molten rare earth metal reacted with the liners which resulted in the contamination of the metal with rare earth oxides.

The very electropositive nature of the rare earth metals limits the materials which can be used in vacuum-casting operations. Experiments conducted by Ahmann (10) indicated that most of the usual oxide refractories are attacked by molten rare earth metals. The same experiments using a tantalum or molybdenum vessel showed no detectable contamination of the rare earth metal. Work conducted by Daane (11) at the Ames Laboratory, on methods of welding tantalum vessels, provided the necessary reaction containers. Using all-tantalum equipment these rare earth metals were prepared by a method which greatly reduced the possibility of oxygen contamination in the product metal.

Yttrium, while not a true rare earth element, lends its name to one of the main sub-groups of the rare earths; it is associated with the heavier members of the group and is difficult to separate from them. From the chemical similarity of yttrium to the rare earths it might be expected that yttrium metal would possess properties similar to those of the rare earth metals.

## HISTORICAL

The first preparation of a rare earth metal was reported, in 1826, by Mosander (12) who reduced cerous chloride with potassium; he studied the reaction of the impure metallic powder with chlorine, bromine, and sulfur vapor. Beringer (13), in 1842, and Wöhler (14), in 1867, substituted sodium as the reductant for cerous chloride. Beringer obtained a powdered product which was identical with that described by Mosander. In 1853, de Marignac (15) produced didymium metal powder by using sodium as the reductant.

In 1890, Winkler (16) reported the reduction of the oxides of lanthanum, cerium, and yttrium with magnesium. A very high-melting slag was formed which prevented the agglomeration and separation of the metal; the resulting product was a pyrophoric powder which contained an excess of magnesium and semi-fused oxides. Matignon (17) and Schiffer (18), in 1900, reduced cerium oxide with aluminum; the former author also reported the reduction of praseodymium oxide with magnesium. Holm (19), in 1902, described the reduction of the oxide with magnesium; in 1904, Muthmann and Weiss (20) used aluminum as the reductant. Most of these early experiments describing the preparation of rare earth metals by reduction of the oxide were carried out in such a manner that the metal, if formed, was highly contaminated with rare earth nitrides and hydrides. The use of aluminum as the reductant probably resulted in the formation of an aluminum alloy.

A patent was issued to Kuhne (21), in 1904, for a modification of the "thermite" method by addition of chlorates to the reaction mixture; the chlorates acted as "boosters" by providing the heat required to fuse the reaction mixture and to allow the rare earth metal to separate from the slag. In 1911, Hirsch (22) reported the reduction of rare earth oxides with aluminum. He also investigated reactions of rare earth oxides with carbon, silicon, and calcium and obtained the corresponding carbides, silicides, or alloys of calcium. Other patents have been issued to Kuzel (23), N. V. Philips' Gloeilampenfabriek (24) and Siemens and Halske (25), who claimed the production of rare earth metals from the oxides, nitrides, and other rare earth compounds by the use of aluminum and zirconium as reductants.

In 1914, Moldenhauer (26) reported that he was not able to prepare the rare earth metals from their oxides by the "thermite" reaction using aluminum, calcium, or magnesium as the reductant. However, he was able to prepare massive cerium metal by adding cerous chloride to a molten calcium bath; the product metal contained 12% calcium and 1.7% iron. He also reduced cerous chloride with aluminum and obtained a stable alloy which prevented the separation of these two metals. Siebert and Korten (27), in 1920, reported that they were not able to obtain rare earth metals by employing the reaction between their halides and carbon at high temperatures. In 1925, Kremers (28) reported that he could not prepare neodymium metal by reducing the chloride with sodium. Zintl and Neumayr (29), in 1933, employed sodium vapor to reduce hot cerous chloride; the powdered reaction product was used directly in further experiments although it was contaminated with sodium chloride. In 1934, Karl (30) reduced cerous chloride in a molten calcium bath and obtained massive metal as an alloy of cerium and calcium. He was unsuccessful in his experiments on the preparation of cerium metal by the reduction of the oxide with silicon carbide or with magnesium.

Attempts to reduce rare earth halides to the metallic state by the reaction with hydrogen have been reported by Jantsch, Skalla, and Grubitsch (31) in 1933. The reaction was conducted under such conditions that any resulting metal alloyed with the gold boat. The reduction efficiency in the best experimental run was less than 50%. In 1930, Jantsch and Skalla (32) had reported that experiments with hydrogen and the trihalides of samarium, europium, and ytterbium proceeded only to the divalent state.

Klemm and Bommer (2), in 1937, prepared the rare earth metals by the reduction of the chlorides with sodium, potassium, or cesium. The reaction was carried out in a glass apparatus at 300°C, and the reaction product was used for x-ray determination of crystal structures without separation of the alkali halide slag material. The above authors

claimed the preparation of all of the rare earth metals except promethium, although longer heating periods and lower temperatures of the order of 250°C, with potassium as the reductant, were required for samarium, europium, and ytterbium.

Trombe and Mahn (33), in 1944, prepared cerium, neodymium and gadolinium metals of 99% purity by addition of the rare earth halide to molten magnesium metal. The heating of the material removed the alloyed magnesium to within an average of 1%. Contamination of the product metal by crucible attack was held to a minimum by conducting the reaction in molybdenum vessels.

Berge and Martin (34), in 1944, prepared cerium metal in yields of 81% on a one-gram scale and 87% on a 50-gram scale. The metal was prepared by reacting cerous chloride with calcium; they also used cerous halogen compounds other than the chloride. Reactions between cerous chloride and magnesium produced no metal; barium as the reductant gave poor yields due to the high melting-point of the slag. At 900°C, lanthanum bromide was reduced on a one-gram scale with a 78% yield. Above the optimum reaction temperature of 996°C lanthanum metal was produced but lower yields resulted.

The latest reported use of an alkali metal as the reductant was by Asprey, Eyring, and Heppler (35), in 1948, who reacted the trifluorides of europium, samarium, neodymium, gadolinium, and lanthanum at 1200°C with sodium vapor. The reaction was carried out in beryllia crucibles and they reported obtaining a grey to black material for which they determined lattice constants. The values of the lattice constants which they reported in each case were too large for the products to be the metals. In 1948, Eyring and Cunningham (36) reported the preparation of praseodymium metal on a small scale by reacting praseodymium fluoride with barium vapor at 1100°C in vacuum.

The methods for producing rare earth metals by the action of an active metal, as the reducing agent, on a rare earth halide have been successful; however, the alkaline earth metals in general have produced massive metal whereas the alkali metals yielded a powdered product. The reduction of rare earth oxides by reactive metals, while theoretically possible, is limited by the high melting-point of the resulting slag. The "thermite" type reaction has not been employed on a commercial scale for the preparation of any of the rare earth metals.

The commercial preparation of cerium has in general been accomplished by electrolytic methods, especially in the case of the commercial grade cerium and "misch metal". The use of the electrolytic method for the preparation of rare earth metals was first reported, in 1875, by Hillebrand and Norton (37) who used the procedure in the preparation of lanthanum, cerium, and didymium metals. Their method consisted of the electrolysis of the molten rare earth chloride contained in a porous cup which was placed in a porcelain crucible filled with a eutectic mixture of sodium chloride and potassium chloride. An iron sheet was used as the anode and the cathode consisted of either an iron or platinum wire. The product was obtained as a mass of finely divided crystals on the cathode. In 1902, Muthmann and co-workers (38,39,40) prepared cerium by the electrolysis of a molten cerous chloride- potassium chloride mixture. The electrolysis was carried out using a carbon cathode which caused the contamination of the product with carbon. A water-cooled copper vessel was used to hold the electrolyte; the solidification of a thin layer of the salt on the walls of the vessel prevented the contamination of the product with copper. Through the use of molten cerous fluoride as the solvent for ceric oxide, they were able to prepare cerium metal by electrolysis but the current efficiency was low. Attempts to substitute potassium fluoride, calcium fluoride, or cryolite as the solvent in this process were unsuccessful; they also found that the presence of silicates in the electrolyte caused the formation of high-melting silicides which interfered with the electrolysis. These workers also prepared lanthanum, praseodymium, and neodymium metals by adding barium chloride to the electrolyte. Impure samarium metal was produced in very low yields by employing a high current density in the electrolysis of a bath of samaric chloride. In 1911, Hirsch (41) electrolyzed a fused bath of cerous chloride in an iron crucible which served as the cathode and a carbon anode; the resistance of the melt was increased by the addition of a mixture of sodium chloride, potassium fluoride, and barium chloride. The cerium metal obtained by this process contained oxygen, carbon, and iron as impurities. The product metal was reported to be purified by the formation of a dilute amalgam with mercury; the impurities were skimmed off and the mercury was removed by distillation. Kremers and Stevens (42) electrolyzed lanthanum onto tungsten electrodes and reported a pure product uncontaminated by tungsten. Trombe (43,44) reported the preparation of lanthanum, cerium, neodymium, and praseodymium metals by electrolytic methods. He employed a molten cadmium anode in the electrolysis of a fused bath of alkali halides containing samaric chloride and was able to obtain a cadmium-samarium alloy. The cadmium was removed from the alloy by distillation and the samarium metal was estimated to contain less than 0.01% cadmium. The preparation of gadolinium metal of comparable purity was reported by the above author.

Hopkins and co-workers (45, 46, 47) electrolyzed non-aqueous solutions of rare earth salts into mercury cathodes at room temperature and reported that the residue, remaining after the removal of the mercury by distillation, was the pure rare earth metal. They prepared lanthanum, cerium, neodymium, and yttrium amalgams from 1 to 3% by weight in the case of the rare earths and 0.6% for yttrium; the samarium concentration in the amalgams was not stated. Derge and Martin (34), in 1944, attempted to separate rare earth metals by distillation of the mercury from rare earth-amalgams in a vacuum. The residual metal contained 5% mercury and other impurities after heating to 1,000°C. This method has not been utilized to any extent by other workers because of the low yield of rare earth metal obtained, due to their low concentration in the amalgam.

Previous workers in the Ames Laboratory (3, 9, 10) were able to prepare rare earth metals by the reduction of rare earth trichlorides with calcium metal in refractory-lined steel bombs. This reaction did not generate enough heat to permit the reaction products to be in the liquid state long enough for the metal to separate. In order to effect a separation of the metal, it was necessary to utilize a side reaction between iodine and calcium; this reaction furnished the required heat to liquefy the products and also served to lower the melting-point of the slag material. The use of refractory oxide liners in these reduction processes caused the product to be contaminated with oxides. This problem was more apparent in the casting operations in which the molten metal was in contact with the oxide refractories for longer periods. Experiments carried out by Ahmann (10), who studied the effect of molten rare earth metals on crucible materials, indicated that neither molybdenum nor tantalum vessels were attacked by these metals. The work of Daane (11) on the preparation of lanthanum, praseodymium and gadolinium metals by the post-heat reduction of the trichloride with calcium, permitted purer rare earth metals to be obtained.

The reaction was carried out in tantalum vessels which eliminated the possibility of contamination of the product metal with rare earth or refractory oxides. The metallurgical work described in this thesis consists of the extension of the above method to other rare earth elements and the increase in the amount of material which could be processed in a single reduction.

# MATERIALS AND EQUIPMENT

## Anhydrous Chlorides

The gadolinium oxide, used in the preparation of the chlorides, was furnished by the Rare Earth Group of the Ames Laboratory. The gadolinium concentrate had been purified by a sodium-amalgam extraction (48) to remove a large proportion of the samarium. The mixed rare earth oxides were further processed by adsorption of their chlorides on a cation-exchange resin, followed by elution with citrate solutions at appropriate pH values (49,50,51). An analysis of the material after the ion-exchange purification process showed 90% $Gd_2O_3$ and 10% $Sm_2O_3$. One additional sodium-amalgam extraction of the above material produced 98% $Gd_2O_3$ containing 2% $Sm_2O_3$. Both of the gadolinium concentrates were used in the experiments described in this thesis. The yttrium oxide was furnished by the Rare Earth Group of the Ames Laboratory. It was a by-product of the concentration of the heavy rare earths from gadolinite ore by ion-exchange methods. An analysis of the material showed the composition to be 90% $Y_2O_3$, and 10% $Dy_2O_3$.

These oxides were converted to the chlorides by dissolving them in concentrated hydrochloric acid. The solution was boiled to drive off the excess water and heating was continued until the temperature reached 135°C; at this point the solution was a thick syrupy liquid. The hot concentrated rare earth chloride solution was poured into a large porcelain evaporating dish. During cooling, the solution was stirred continuously in order to obtain a fine crystalline powder.

The hydrated rare earth chloride was loaded into a Pyrex drying tube three inches in diameter and 36 inches long. A 40/50 standard taper connection was sealed on the outlet end of this tube to facilitate the assembling of the drying system. The loaded tube was placed in a chromel-wound resistance furnace which was 30 inches long and five inches in diameter. The procedure of Kleinheksel and Kremers (52), which consisted of heating the crystalline hydrate in an atmosphere of anhydrous hydrogen chloride gas at reduced pressure, was followed in preparing the anhydrous chlorides. This method has been reported as being the most satisfactory for the preparation of the pure anhydrous halides (53 p.29). The usual method used in the drying procedure consisted of slowly raising the temperature of the hydrate from below 80°C to above 400°C while hydrogen chloride gas was passed through the apparatus against a pressure of five cm of Hg. Anhydrous rare earth chlorides were obtained in 24 to 36 hours. The hydrated chloride was not permitted to melt, since this would cause the formation of the rare earth oxychloride.

The anhydrous hydrogen chloride gas was procured from the Matheson Company; each cylinder contained 15 pounds of the gas. The tank of hydrogen chloride gas was connected through a small drying tube to the drying apparatus. In order to remove the residual hydrogen chloride gas, the drying tube was connected through a bubbler trap system to a glass water-aspirator which served to maintain the pressure in the apparatus at approximately five cm of Hg.

## Crucibles

The tantalum reduction crucibles used in the initial experiments were obtained from the Fansteel Metallurgical Company. These crucibles were drawn from a single sheet and were of seamless construction. The crucible dimensions were one-inch inside diameter and three inches long and had a capacity of approximately 40 grams of the reaction mixture. These crucibles were very satisfactory except for the difficulty encountered in removing the metal from the crucible. Before any extensive program of metal production could be undertaken, it was necessary to fabricate crucibles of tantalum that could be used for reduction and then discarded when the metal was removed.

The crucibles were constructed of tantalum foil with welded bottoms and side seams by a process developed by Daane (11) in the Ames Laboratory. The method of fabrication of the crucibles involved folding a sheet of tantalum foil on a circular brass mandrel one and one-sixteenth-inch outside diameter, as shown in Figure 1, and crimping the side seam with pliers into a simple sheet-metal joint. The mandrel and folded cylinder were placed in the welding apparatus shown in Figure 2. The welding system was evacuated to less than 100 microns pressure and flushed with argon gas; the welding operation was carried out in an argon atmosphere using a direct current arc. The brass mandrel with the folded crucible acted as the positive electrode; a cored, pointed graphite rod was used as the cathode and was fabricated from 6.4 mm micro-projection arc electrodes furnished by the National Carbon Company.

The current required for a smooth weld depends on the thickness of the foil employed. In this work, crucibles of 0.001-inch, 0.002-inch, and 0.005-inch foils were fabricated requiring 6, 9.5, and 12 amperes direct current, respectively. The crucible bottoms were hammered out of 0.002-inch foil using a stamping die. The bottoms were approximately 3/8 inch deep. These stamped discs were fitted inside the welded cylinder, the excess being folded outside. In order to insure a tight fit, the bottoms were crimped on with pliers, care being taken not to punch holes in the bottoms. The assembled crucible was placed in the

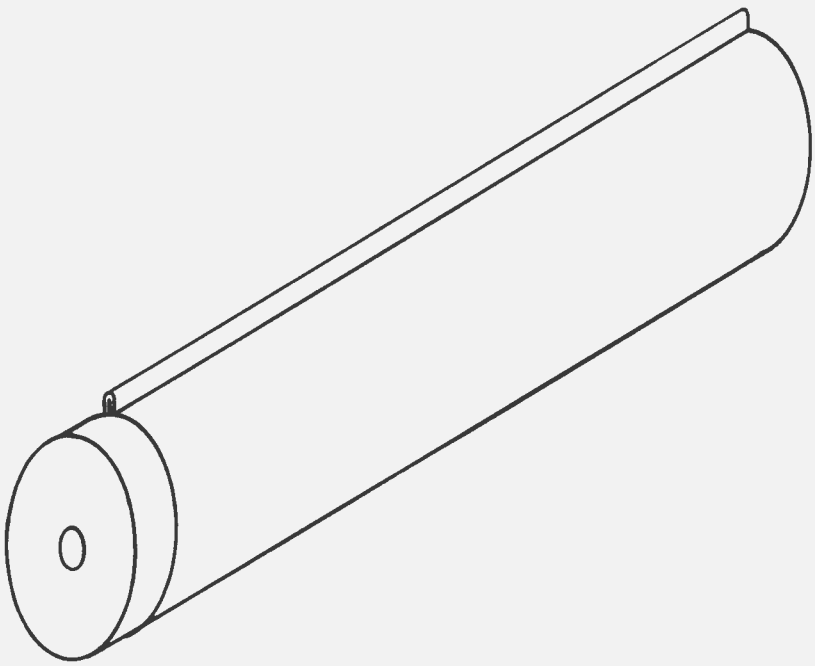

Fig. 1 — Brass mandrel with folded tantalum foil cylinder.

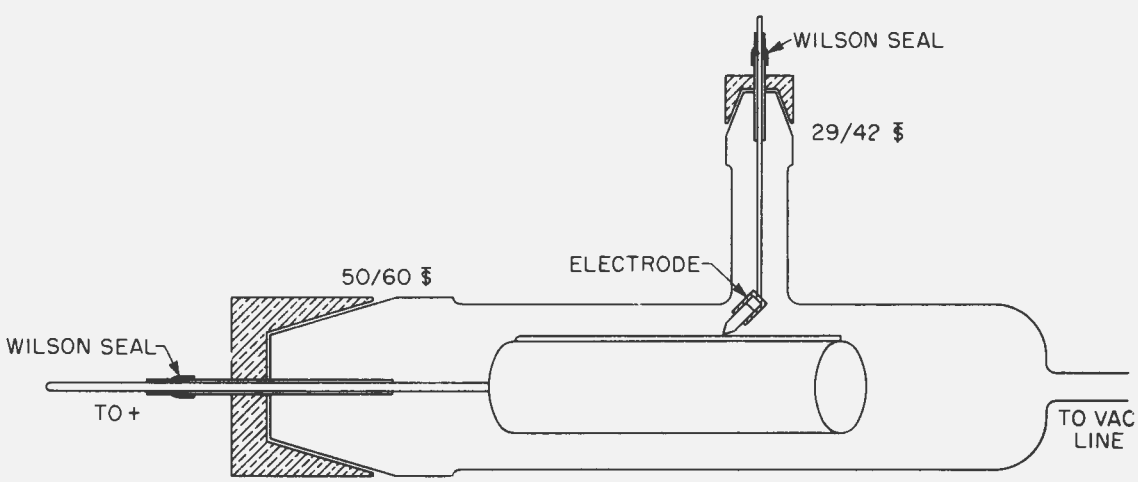


Fig. 2 — Diagram of welding apparatus.

welding apparatus and the system alternately evacuated and flushed with argon. The welding operation was carried out as before, exercising care in order to effect a leak-proof seal, especially in the region of the side seam. The completed crucible was tested for leaks by immersion in acetone and blowing air into the crucible. The standard size employed in most of these experiments was five inches long and one and one-sixteenth inches inside diameter.

## Reduction Apparatus

The preparation of the rare earth metals was carried out in an apparatus which could be evacuated and filled with an inert gas such as argon or helium (3). The arrangement of the equipment, shown in Figure 3, consisted of a reduction tube which was connected to a vacuum pump through an air-cooled, welded, brass trap. The reduction tubes were of fused silica five inches inside diameter and 30 inches long, with one end closed, and were obtained from Amersil Company. The tube was connected to the vacuum system through a water-cooled vacuum head, the leak-proof seal being effected by a round rubber gasket and Celvarene vacuum grease. In order to observe the course of the reaction and to measure the temperature, a metal tube through the vacuum head was covered with a plane sight glass sealed in place with Pyseal Wax manufactured by the Fisher Scientific Company. Attached to the brass trap was a three-way stopcock, one arm of which was connected to a Model 507 thermocouple vacuum gage used in conjunction with a Model 710 Thermocouple-Ionization gage controller; both of these instruments were purchased from the National Research Corporation. The other arm of the stopcock was utilized as the inlet for the helium gas which flowed through the system during the reaction and cooling periods. The vacuum pump was connected, as indicated, at the bottom of the trap; the pump employed was a Cenco Hyper Vac pump.

The details of the reaction tube containing the tantalum crucible are shown in Figure 4; since the thin-walled crucibles did not prove to be very efficient as inductors, it was necessary to include a tantalum crucible, two-inch inside diameter and five inches long, procured from the Fansteel Metallurgical Company. This larger crucible acted as the heating element in conjunction with a water-cooled induction heating coil fabricated of copper tubing connected to a 30 KW Ajax High Frequency Converter, manufactured by the Ajax-Northrup Company. The large tantalum inductor was placed in a sintered magnesium oxide crucible prepared by the Ceramics Shop of the Ames Laboratory; this, in turn, was surrounded by other suitable refractory material necessary to protect the tube from excessive loss of heat through radiation. A cover disc of

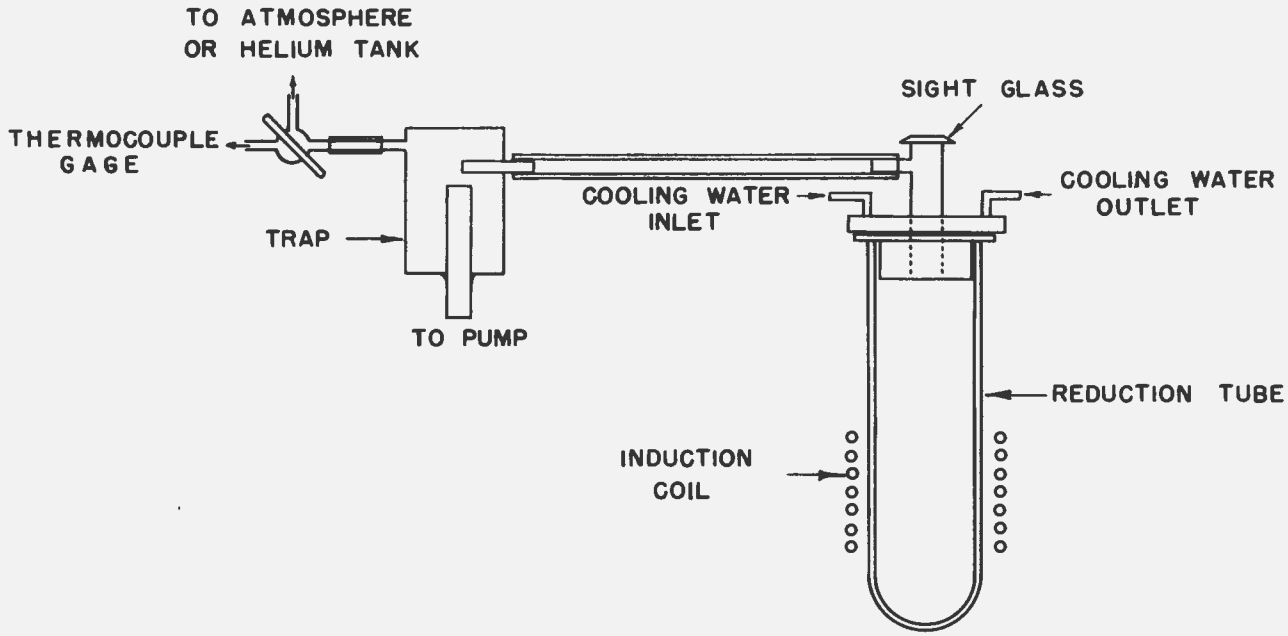


Fig. 3 — Diagram of reduction and casting apparatus.

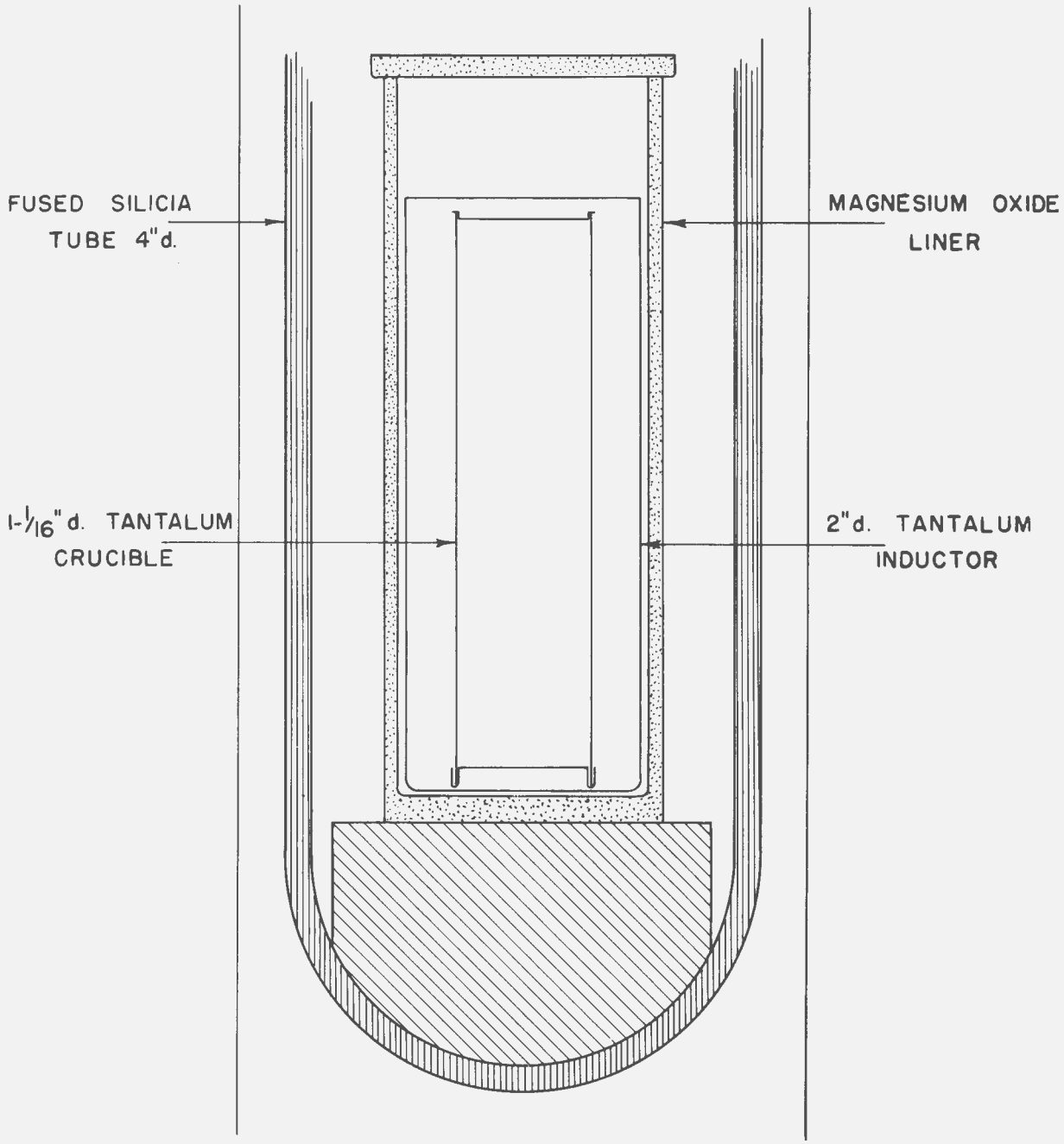


Fig. 4 — Diagram of combustion tube.

sintered magnesium oxide, with a hole in the center, was employed to further reduce radiation losses from the reaction crucible.

The reduction system as described above has proved to be a very versatile assembly. In the experiments here reported it was necessary to remove any residual amounts of gas in the reduction chamber by heating the crucible to 1200°C in vacuum. All temperatures in these experiments were measured by an optical pyrometer purchased from Leeds and Northrup Company.

## Calcium

The preparation of the rare earth metals by thermal decomposition of anhydrous rare earth chlorides by an active metal necessitates the use of a very pure reductant in order to prevent contamination of the product metal by impurities in the reductant. Calcium was used as the reductant in all of these experiments, because of the ease in handling and the good storage stability of the metal. The calcium was prepared by methods developed in the Ames Laboratory (54) by distilling the crude calcium obtained from Dominion Magnesium Ltd. Product metal from the distillation consisted of large aggregates which were reduced by a number of steps to the size suitable for the reduction process. The final size was such that the metal passed through a 10 mesh per inch screen, but was retained on a 50 mesh per inch screen. This sieving served to remove any loose calcium oxide film which was discarded in the "fines"; the final product was stored in argon gas to inhibit further oxidation.

The calcium metal obtained by the above process provided a very reactive and easily handled reductant of the desired purity. Typical analyses of the calcium metal showed the presence of the following impurities in parts per million; iron, 40; manganese, 20; nitrogen, 50; boron, less than 1; cadmium, less than 1; aluminum, 15; magnesium, 400; carbon, 250; sodium, less than 50; potassium, less than 50; lithium, less than 20.

## Reaction Mixture

The anhydrous gadolinium chloride, prepared by the method described above, was mixed with calcium metal in a dry-room. The reaction for the preparation of gadolinium metal is

$$GdCl_3 + 1.5\ Ca \longrightarrow Gd + 1.5\ CaCl_2 .$$

A 10% excess of the theoretical amount of calcium was employed in all of the experiments. The anhydrous gadolinium chloride was weighed out in the dry-room since the anhydrous rare earth chlorides are very hydroscopic. It was usually necessary to grind the lumps of anhydrous chloride to a fine powder in order to ensure uniform mixing with the reductant. A clean dry reagent jar was used to mix the charge by tumbling the reaction mixture.

In order to increase the quantity of metal which could be produced in a given size crucible, the mixed charge was placed in a die and subjected to a pressure of 5,000 pounds per square inch. A hydraulic press was employed in this compacting operation; the assembly is shown in Figure 5-A. The pressed charges fit into the one and one sixteenth-inch inside diameter crucibles employed in most of these reductions (see Figure 5-B). The quantity of charge accommodated by the crucible is increased 50% by the compacting process. An added advantage realized in compacting the charge is that on evacuation of the reduction system, the pressed charges have little tendency to blow around when the pump is initially started.

## EXPERIMENTAL RESULTS

### Gadolinium

#### Reduction

The reduction apparatus had been previously degassed by heating the two-inch inside diameter tantalum crucible to a temperature of 1200°C in a vacuum. After cooling, the system was filled to atmospheric pressure with helium gas. The pressed charge, which had been prepared and loaded in a welded tantalum crucible as described above, was placed in the reduction apparatus. The system was evacuated to 25 microns pressure and then filled with helium gas. This operation was carried out twice in order to remove any residual gases which might react with the tantalum crucibles or with the rare earth metal.

The reduction was carried out in an atmosphere of helium with a slow stream of the gas entering the system both during the heating and while the crucible was cooling to room temperature. The reaction was initiated by heating the reaction mixture in an induction furnace; the power input was set on the lowest operating value of the 30 KW Ajax Converter. The heating was conducted at a slow rate until the reaction started. After the charge had fired, as indicated by a temperature increase in the crucible, as observed through the sight glass, the power input was increased. In this post-heat method, the temperature of the reaction vessel could be held at a value above the melting-point of the metal

Fig. 5-A — Hydraulic press.

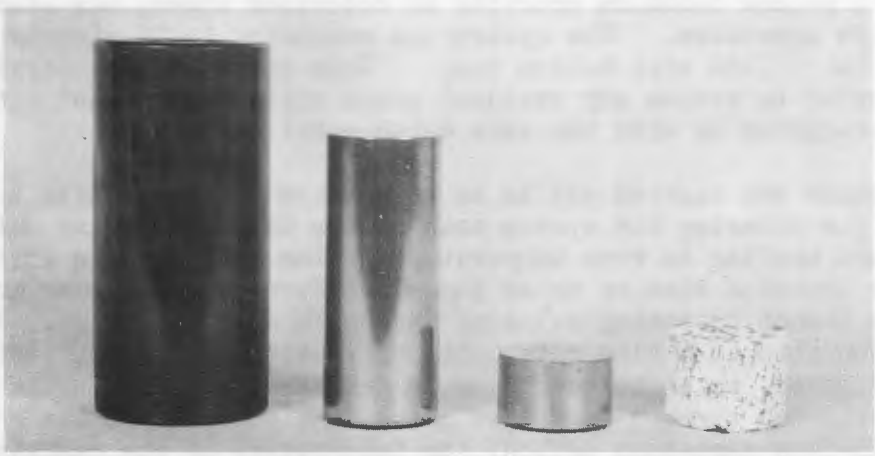

Fig. 5-B — Pressing die and compacted charge.

being produced. In the case of gadolinium, the temperature required to produce massive metal was slightly in excess of 1300°C. The temperature was held above the melting-point of the metal and slag in order to insure separation of the metallic gadolinium in the bottom of the crucible.

After cooling, the tantalum crucible was removed from the system. The shrinkage of the crucible at the bottom, due to the contraction of the metal ingot, is shown in Figure 6. The slag was removed from the crucible by washing in distilled water or the tantalum crucible was peeled off down to the metal. The slag had a dark brown color; when placed in distilled water a red-brown solution resulted; The latter color is a characteristic of samarous ion.

Previous attempts to prepare samarium metal by bomb-reduction (10) and by the post-heat method (3), resulted in the preparation of samarous chloride instead of the metal. Since pure samarium chloride was not reduced to the metal in this reduction process, an experiment was conducted in an attempt to separate gadolinium from samarium by the preparation of gadolinium metal. An analysis of the anhydrous chloride indicated its composition to be 98% $GdCl_3$ and 2% $SmCl_3$. The analysis of the product separated from the reduction showed that the slag contained practically all of the samarium present in the original anhydrous chloride. The metal was cast and the analysis indicated the presence of 0.06% $Sm_2O_3$, which is the lower limit of detection by the spectrographic method used. Later experiments conducted with material containing 90% $Gd_2O_3$ and 10% $Sm_2O_3$ gave the same results as those noted above, showing that by the reduction of this latter material it was possible to prepare pure gadolinium metal, thus eliminating the second sodium-amalgam extraction in the purification process.

The results of the reduction process are tabulated in Table I. The percentage yield was calculated on the basis of the gadolinium chloride content in the total weight of anhydrous chloride in the reaction mixture.

Casting

The rare earth metals prepared by the post-heat method as outlined above, usually contained about 5% calcium metal as determined by spectrochemical analysis. The residual calcium was removed by heating the biscuit metal in a vacuum or in an inert atmosphere. In all of these experiments the casting operation was carried out in vacuum to facilitate the distillation at a lower temperature. The vacuum system which was used for the casting of rare earth metals was the same type as shown in Figure 3. During the purification process, a vacuum of less than 100 microns was maintained by raising the temperature slowly until all of

TABLE I

Results for the Production of Gadolinium Metal

| Total wt. of charge (grams) | Wt. of anhydrous chloride (grams) | Wt. of metal produced (grams) | Yield (%) |
|---|---|---|---|
| 54.0 | 44 | 26.0 | 100 |
| 300.0 | 238 | 80.0 | 56* |
| 282.0 | 225 | 125.0 | 100 |
| 37.6 | 30 | - - | --* |
| 50.5 | 40 | 22.5 | 100 |
| 50.5 | 40 | 21.5 | 97 |
| 225.0 | 180 | 96.5 | 100 |
| 50.5 | 40 | 22.5 | 100 |
| 140.1 | 111 | 63.0 | 100 |

*Low yield was due to the fact that the temperature was too low to permit the agglomeration of the metal.

the calcium had been removed. At a temperature of 1200°C, as measured visually by an optical pyrometer, the calcium was removed rapidly; by previous experiments it had been determined that the remaining calcium was present to the extent of less than 0.1% in the rare earth metal.

The reactive nature of the rare earth metals required a preliminary treatment of the apparatus to be used in casting operations. The sintered magnesium oxide liners were heated to a red heat in a muffle furnace to remove the carbon that remained from the fabrication process. The crucible assembly, shown in Figure 4, was heated in vacuum to remove the absorbed gases which might react with the molten rare earth metal.

Previous experiments reported by Ahmann (10) indicated that molten rare earth metals attacked oxide refractories at the temperatures required to remove a large portion of the calcium which remained from the reduction process. However, tantalum casting-vessels were relatively inert to molten rare earth metals. In all the experiments reported in the present thesis, tantalum crucibles were employed in order to obtain metal which had had no contact with oxide refractories and showed that the contamination of the product metal by the formation of rare earth oxides had been held to a minimum.

The general appearance of freshly cast gadolinium metal is a silver-grey color as would be expected from previous work with the other rare earth elements. This metal, in contrast to certain of the other metals, notably cerium, can be sawed or turned on a lathe without sparking or burning. Gadolinium metal resists oxidation in the atmosphere to a very marked degree when compared to lanthanum or cerium and can be kept in air for a long time without tarnishing to any extent.

A ring of gadolinium was cooled below the Curie point, which is somewhat below room temperature; under these conditions gadolinium metal changes from a paramagnetic to a ferromagnetic material. Figure 7 shows these properties by the suspension of the ring on an alnico magnet.

Preparation of powder

The problem of preparing gadolinium powder was investigated because metallic powders can be useful in solving certain metallurgical problems. The conditions for mixing the charge and for preparation for reduction are identical with those described for preparation of massive metal. The heating process was initiated as in the regular reduction except that the temperature was raised very slowly after the charge had fired. The temperature of the reaction vessel was maintained at 800°C for ten minutes.

After cooling to room temperature, the crucible was removed. The reacted mass was incompletely fused and had the appearance of a black cinder. The reaction mixture in the crucible was leached with distilled water and the red-brown color of the washings indicated that the samarium was not reduced to metal. The reaction product was removed from the crucible and ground in a mortar with pestle. Successive washing and grinding operations were carried out until most of the calcium chloride was removed. The residue from the reduction was ground until it passed a 60-mesh screen. Although particles of this degree of fineness were more rapidly oxidized, the grinding was necessary to remove most of the slag from the metal powder.

Fig. 6 — A typical reduction crucible with constriction near the bottom due to the metal produced.

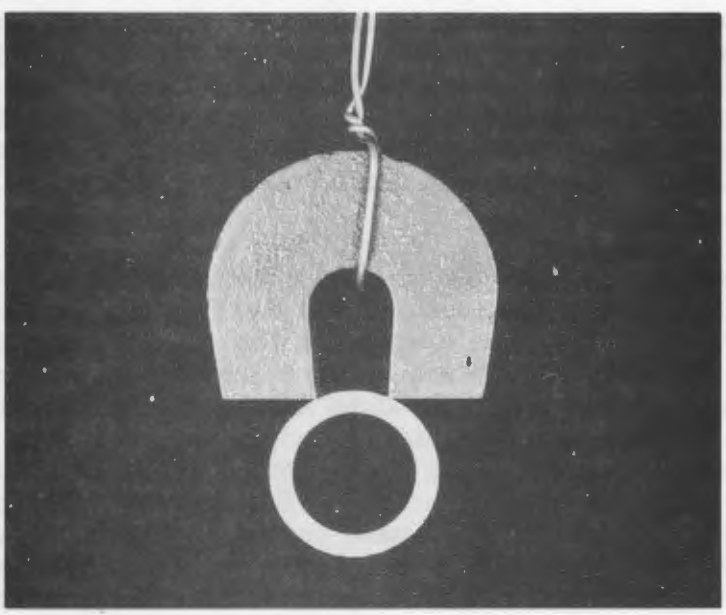

Fig. 7 — Ring of cast gadolinium metal suspended by a magnet.

The particles were washed with acetone to remove most of the water and to inhibit the rapid oxidation. The ferromagnetic properties of the gadolinium were used to separate the powder from the slag. Solid carbon dioxide was added to the acetone washings to lower the temperature. When the mixture had cooled sufficiently, an alnico horseshoe permanent magnet was introduced into the beaker to effect the separation from the remainder of the slag. The magnet with the adhering gadolinium powder was allowed to warm up to room temperature, at which point the attraction was less and the gadolinium powder could be more easily removed from the magnet. The 40 grams of powder obtained were washed in ether, dried and stored in a helium atmosphere. The yield, which was calculated on the quantity of gadolinium chloride present in the reaction mixture, was 63.5%.

## Yttrium

### Reduction

Previous attempts to prepare metallic yttrium by reduction with calcium metal (10,55) yielded a grey-black powder that was intimately mixed with the slag. This metallic powder was separated from the mixture by washing the reduction product with water but the fine particles were rapidly oxidized. Attempts to press this powder into brickettes for subsequent melting or sintering in vacuum were not sucessful even at temperatures far in excess of the reported melting-point of yttrium metal (55). In the initial experimental attempts to produce gadolinium metal, low yields were obtained with some small droplets of metal in the slag. These results indicated that heating the reaction mixture to high temperatures for a longer period would increase the yield by causing the reaction products to become more fluid and enabling the heavier metal droplets to agglomerate more readily. It was assumed that by subjecting the reaction mixture in the case of an yttrium reduction to a temperature of 250 to 300°C, above the reported melting-point, that the metal would collect in the bottom of the reaction crucible.

The procedure for the preparation of yttrium metal by the post-heat reduction technique was the same as that outlined previously for the preparation of gadolinium metal. After the initial reaction had taken place, as indicated by a sharp rise in temperature of the reaction crucible, the temperature of the two-inch tantalum inductor was increased rapidly to 1750°C or slightly higher. This process of heating the reaction mixtures to a point 250 to 300°C above the melting-point was determined experimentally in the case of gadolinium by noting that at this value the theoretical yield was obtained. In the preparation of

yttrium metal, however, this process was complicated by the fact that 1750°C is above the boiling point of the slag and also above the boiling-point of the calcium metal which is employed as the reductant. This accounts for the low yield in the case of yttrium which was not encountered in the preparation of the rare earth metals which have lower melting-points.

The preparation of yttrium metal by the post-heat method was conducted using 30 grams of anhydrous yttrium chloride and a 10% excess of the necessary quantity of calcium metal to complete the reaction. From this reduction process 9.5 grams of metal resulted. The yield, which was calculated on the basis of the total quantity of rare earth chloride in the reaction mixture was 69.5%. Previous attempts to prepare yttrium metal resulted in a product which ranged from a finely-divided powder mixed with the slag to large droplets of metal in the slag but massive metal was produced only in the experiment reported above.

Casting

The procedure, used in casting yttrium metal, was the same as outlined in the discussion of gadolinium metal. Due to the higher melting-point of yttrium it was necessary to heat the metal to 1700°C in order to obtain a well-formed pellet.

## SUMMARY AND CONCLUSIONS

The techniques described in the present study have been successfully employed in the preparation of gadolinium metal, gadolinium powder and yttrium metal. The method possesses the following advantages:

1. The magnitude of the charge is limited only by the size of the tantalum reaction vessels which can be fabricated. Reductions were carried out on a 50-gram scale, a 140-gram scale, a 225-gram scale, and a 300-gram scale.

2. The quantity of reaction mixture in the one and one-sixteenth-inch inside diameter crucibles can be increased by compacting the charge into one-inch pellets; increases of up to 50% have been effected.

3. Under optimum conditions resulting yields approached the theoretical quantity of gadolinium present in the chloride.

4. Experimental reductions which proved unsuccessful did not present the recovery difficulties which had been encountered in the previous reduction method. The reaction mixture does not fuse to a porous magnesium oxide liner thereby introducing large quantities of magnesium and complicating the recovery of the rare earths present.

5. The presence of helium in the reduction tube minimizes the possibility of formation of rare earth oxides or of rare earth nitrides in the metals.

6. Separations of samarium from gadolinium have been effected by the reduction of gadolinium to the metal.

7. Yttrium metal was produced by this method but the percentage yield was not as high as that of the rare earth metal investigated.

8. The method of preparing rare earth metals yields a product of very high purity because the reaction was carried out in containers which were not attacked by the metal produced and the presence of an inert atmosphere minimized the possibility of contamination due to oxide or nitride formation.

The method presented in this thesis can undoubtedly be extended to the preparation of the heavier rare earth metals but the process will be complicated by the melting-point of the metal which increases with increase in atomic weight. The slag resulting from the production of the heavy rare earths would boil at a temperature below that required to cause the metal to agglomerate; it may be necessary to employ the rare earth fluorides with calcium in the reduction process in order to obtain calcium fluoride as the calcium reaction product. Calcium fluoride has a boiling-point substantially above the temperature required to cause agglomeration of the metal.

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